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Treatment of wastewater from the production of meat and bone meal by the Fenton process and coagulation

Agnieszka Makara[1,*], Zygmunt Kowalski[2], Piotr Radomski[1], Piotr Olczak[2]

[1]Cracow University of Technology, Faculty of Chemical Engineering and Technology, Warszawska 24, 31-155 Cracow, Poland
[2]Mineral and Energy Economy Research Institute Polish Academy of Sciences, Wybickiego 7, 31-261 Cracow, Poland
[*]Corresponding author: e-mail: agnieszka.makara@pk.edu.pl

Wastewater from the production of meat and bone meal, due to the high load of organic matter and suspended solids, is a significant problem in the process of its treatment. In this work, we examined the method of treating this wastewater using coagulation with hydrogen peroxide and the Fenton process. Treatment variants included the use of variable Fe^{2+}/H_2O_2 ratios of 1:5–1:30, variable doses of 3–18.0 g/L H_2O_2, and 5–10 mL/L of coagulant PIX 113. The calculated reduction degrees showed that, regardless of the treatment variant used, the greatest reduction was obtained for turbidity (100%), phosphorus (99%), followed by color (97%), chemical oxygen demand (70%), and Kjeldahl nitrogen (48%). The proposed treatment options can be used as a preliminary stage in treating wastewater from the production of meat and bone meal.

Keywords: wastewater, meat and bone meal, Fenton process, coagulation, chemical oxygen demand.

INTRODUCTION

Approximately 18 Mt/y of meat waste is generated in the European Union, which is mainly processed into meat and bone meal (MBM). The EU produces 4.5 Mt/y of MBM, used typically as biofuel[1, 2] and mineral-organic fertilizers. The product of MBM combustion could also be used as fertiliser[3, 4]. The United States renders 2.1 M metric t/y of bovine, porcine, or mixed species MBM[5]. In Poland, the amount of meat waste is estimated to be 1 Mt/y. These were processed into MBM, of which production was 400,000 t/y. Meat and bone meal are currently used as biofuel[6], but also as soil improvers (MBM from category III waste) or mineral-organic fertiliser[7, 8]. The raw materials used for MBM production contain about 40% moisture, and from their dry mass, 90% meat and bone meal and 10% fat also used as biofuel were obtained[9, 10].

MBM production in Poland generates about 1 Mm^3/y of wastewater with a very high content of organic compounds, and up to 25 g/L chemical oxygen demand (COD). The high content of organic compounds as well as phosphorus and nitrogen generates problems related to conventional biological wastewater treatment. Therefore, there is a need to pre-treat wastewater from meat and bone meal production by mechanical and chemical methods before applying the biological method. Most often, in this case, chemical treatment methods are used, mainly coagulation to reduce the COD of the sewage before further treatment. In addition to reducing COD, chemical methods of wastewater treatment reduce suspended solids, phosphorus, BOD, and bacteria[11, 12, 13]. The combination of filtration and flotation enables a reduction of BOD values (by 70%), the number of nitrogen compounds (by 55%), phosphorus compounds (by 70%), and fat residues (by 85%)[12]. In the treatment of meat industry wastewater, to support the separation and flotation processes, precipitants are used, especially coagulants and flocculants.

In earlier work, Makara et al.[13] studied the process of wastewater treatment from MBM production containing an average of 8,600 mg/L COD, upon removal of solids on stationary and rotary sieves, using variable doses of Scanpol 40, PIX 113, PAX 18, and Ekoflok coagulants. PIX 113 coagulants based on iron(II) sulfate provided the most effective reduction of COD by 72.9%, and the reduction of color and turbidity by 96.8% and 99.2%. Aggregates formed during the coagulation process can be removed using sedimentation and filtration, and the supernatant is directed to the next processing step, e.g. biological treatment, or it is directly released into the external environment[14, 15]. Advantages of coagulation include simplicity of the process and low energy requirements[16, 17].

In the study by Bohdziewicz et al.[18], the meat industry wastewater was treated in a system linking the processes of coagulation, a biological treatment using the activated sludge method, simultaneous precipitation of phosphorus, and reverse osmosis. The treated wastewater could be released into the natural water reservoirs or it was possible to use it again in the technological cycle. The paper by Bohdziewicz and Sroka[19] presents a method for the treatment of meat industry wastewater using hybrid processes in the following combinations: ultrafiltration--reverse osmosis, coagulation–reverse osmosis, and coagulation-ultrafiltration-reverse osmosis. The proposed method made it possible for the treated wastewater to be reused in the production cycle.

The results of meat wastewater treatment with coagulants and so-called "coagulant aids" were described[20]. These showed that aluminum sulfate was nearly twice as effective in the presence of alumina powder due to the fact that the aggregation and sedimentation speed can be greatly enhanced.

Treatment of meat industry wastewater containing 13,000 mg/L COD was studied using three ferric salts as coagulants in conjunction with four different polymers as flocculants, by batch column flotation[21]. The effluent was characterized in terms of turbidity, total solids TS, BOD, and COD contents. The treatments achieved reductions of total solids by up to 85%, as well as BOD and COD by 62.0–78.8% and 74.6–79.5%.

For the treatment of wastewater from the meat industry and MBM production, advanced oxidation technologies (AOTs) are used, which include the Fenton reaction. The oxidizing agents in the Fenton reaction are hydroxyl radicals. Ferrous ions catalyze the transformations, in which harmless by-products are formed (including water and oxygen)[22, 23]. The effectiveness of Fenton's reaction depends on the H_2O_2 concentration, Fe^{2+}/H_2O_2 ratio, pH, temperature, reaction time, and concentration and type of impurities. Fenton's reagent, apart from the oxidation of compounds, performs a coagulant function. Coagulation removes residual impurities that have not been oxidized in the reaction[24].

In the study by De Sena et al.[25], the effectiveness of the meat wastewater treatment by dissolved air flotation (DAF), followed by advanced oxidation processes (AOPs) using photo-peroxidation (H_2O_2/UV) and photo-Fenton reactions, was evaluated. Results of BOD and COD reduction varied between 54–67% and 74–82%. For total solids (TS) and volatile solids (VS) reductions of up to 68% and 84% were achieved.

The study by Kwarciak-Kozłowska et al.[26] compared the efficiency of the treatment of wastewater from slaughtering and meat processing containing an average of 2,450 mg/L COD, in the coagulation process and in the oxidation process using Fenton's reagent. COD removal with the use of Fenton's reagent (78%) was higher by 10% on average compared to the use of coagulant PIX 113. The total organic carbon (TOC) and total nitrogen (TN) removal efficiency using Fenton's reagent were higher by 13% and 40.5% respectively when compared to the coagulation process only.

The available papers mainly concern the treatment of wastewater from the meat industry, while the presented work focuses on the treatment of wastewater from the processing of animal waste and by-products into meat and bone meal. In plants producing MBM, the generated wastewater is a problem due to the very high load of organic pollutants and the resulting threat to the environment. The physicochemical composition of sewage from MBM production can be very diverse depending on the type of MBM production technology and the raw material used. Treatment of this wastewater is difficult and requires the choice of several stages of purification. Chemical and/or biological purification methods are usually used. The first stage is the typical mechanical treatment carried out on the Huber sieve to remove solids and fats. The solid waste from mechanical treatment is recycled into MBM production[27]. The next stage of wastewater treatment uses coagulation and flocculation-assisted flotation, and the last stage is biological treatment. The degree of wastewater treatment depends on the treatment technology used and the intended use of the treated wastewater. This can be discharged into water and sewage systems, or also used, for example, to irrigate arable fields.

The goal of the research was to determine the effect of the coagulation and Fenton reaction, carried out with the use of two sources of iron ions ($FeSO_4 \cdot 7H_2O$ and PIX 113) and the oxidizing agent in the form of H_2O_2, on the effectiveness of the treatment of wastewater from the production of meat and bone meal.

MATERIAL AND METHODS

The treatment tests were carried out on wastewater from a MBM production plant located in northern Poland.

Table 1 shows the physicochemical characteristics of the wastewater from the MBM unit after mechanical treatment – RE used in tests. Tests of the MBM wastewater treatment using the Fenton process and coagulation were carried out without preliminary adjustment of the wastewater pH, to eliminate the additional acidification stage.

Wastewater was treated in the Fenton process, using $FeSO_4 \cdot 7H_2O$ and H_2O_2 as reagents, as well as Kemira PIX 113 coagulant. $FeSO_4 \cdot 7H_2O$ was produced by Merck, while the 30% H_2O_2 solution was treated by POCH. The Kemira PIX 113 coagulant, used as a source of iron ions, was in the form of a dark brown liquid with a density of 1.54 g/L, containing in weight %: 35–50% $Fe_2(SO_4)_3$, 0.1–1.5% $FeSO_4$ and <0.25% $MnSO_4$. Wastewater neutralization was carried out with a solution of lime milk, and calcium oxide was purchased from the Chempur company.

Table 1. Physicochemical parameters of wastewater from the MBM unit after mechanical treatment – RE

Parameter	Unit	Content in RE*
Turbidity	[NTU]	205
Color	[mg Pt/L]	3,260
pH	–	6.68
COD	[mg O_2/L]	11,544
Kjeldahl nitrogen	[mg/L]	1,110
P	[mg/L]	109.63
Ca	[mg/L]	69.000
Mg	[mg/L]	19.900
Fe	[mg/L]	1.300
Zn	[mg/L]	0.497
Mn	[mg/L]	0.097
Ni	[mg/L]	<0.070
K	[mg/L]	259.000
Cu	[mg/L]	<0.080
Cd	[mg/L]	<0.040
Cr	[mg/L]	<0.090
Pb	[mg/L]	<0.700
Co	[mg/L]	<0.080

*RE – raw effluents after mechanical treatment

Wastewater treatment was carried out at room temperature using four variants: Variant I – constant dose of $FeSO_4 \cdot 7H_2O$ (3 g/L) and variable doses of H_2O_2 (3–18 g/L); Variant II – variable doses of $FeSO_4 \cdot 7H_2O$ (3–10.5 g/L) and variable doses of H_2O_2 (6–21 g/L); Variant III – fixed doses of PIX 113 coagulant (7.7 g/L) and variable doses of H_2O_2 (3–18 g/L); Variant IV – variable doses of PIX 113 coagulant (7.7–15.4 g/L) and fixed doses of H_2O_2 (10 g/L).

Each of the series of tests carried out included six 100 mL wastewater samples, to which $FeSO_4 \cdot 7H_2O$ or PIX 113 coagulant was added and the slurry was stirred in a magnetic stirrer for 15 minutes. Then hydrogen peroxide was added and mixing was continued for another 60 minutes, after which the samples were allowed to stand for about 30 minutes and neutralized with a 5% solution of lime milk to a pH of 7–8. Next, the slurry after neutralization was filtered through a qualitative cellulose filter. In the liquid fractions, COD, color, turbidity, pH, temperature, and Kjeldahl nitrogen, P, Ca, Mg, Fe, Zn, Mn, Ni, K, Cu, Cd, Cr, Pb, and Co were determined.

The value of chemical oxygen demand was determined by the dichromate method in accordance with the PN--ISO 6060: 2006 standard and the mineralization of the samples was carried out in a 9-station M9 mineralizer by WSL[28]. The color was determined in accordance with the PN-EN ISO 7887: 2002 standard, in the platinum-cobalt scale, at the wavelength λ = 436 nm[29]. The nanocolor UV/VIS spectrophotometer by Macherey-Nagel was used for color measurements. Turbidity measurements (wavelength λ = 860 nm), according to PN-EN ISO 7027: 2003[30], were performed using a nephelometer built into the Nanocolor UV/VIS spectrophotometer by Macherey-Nagel. The pH value and temperature were measured with a Mettler Toledo Seven Easy S20-K pH meter. The content of total phosphorus after oxidation with potassium peroxide sulfate was determined by the spectrophotometric method according to EN ISO 6878: 2004[31]. The measurements were made using the Nanocolor UV/VIS spectrophotometer by Macherey-Nagel at the wavelength λ = 880 nm. Kjeldahl nitrogen, being the sum of the ammonium and organic nitrogen, was determined according to PN-EN 25663: 2001[32]. The Kjeldahl nitrogen determination set consisted of the VELP DK6 electric mineralizer, in which the sample was mineralized with selenium, and the VELP UDK 132 steam sample distillation apparatus. The content of elements Ca, Mg, Fe, Zn, Mn, Ni, K, Cu, Cd, Cr, Pb, and Co were determined by Atomic Absorption Spectrometry using the Perkin Elmer 370 apparatus.

SEM/EDS techniques for the analysis of selected sediment samples were performed using a Hitachi TM3000 scanning electron microscope.

RESULTS AND DISCUSSION

Tables 2–5 present the results of physicochemical analyses of the liquid fractions (filtrates) obtained after MBM wastewater treatment and the detailed parameters of the treatment process used.

In Variants I and II, the Fenton process was used, in which the decomposition of H_2O_2 was catalyzed by ferrous ions from $FeSO_4 \cdot 7H_2O$, and then H_2O_2 was decomposed to ·OH, and the production of other radicals that could completely oxidize the organic matter was started.

Table 2. Results of physicochemical analysis of wastewater samples from MBM production treated using the Fenton process, with a variable mass ratio of Fe^{2+}/H_2O_2 – Variant I

Mass ratio	Variant I					
Fe^{2+}/H_2O_2	1:5	1:10	1:15	1:20	1:25	1:30
Doses of reagents/pH						
$FeSO_4 \cdot 7H_2O$ [g/L]	3.0	3.0	3.0	3.0	3.0	3.0
H_2O_2 [g/L]	3.0	6.0	9.0	12.0	15.0	18.0
Lime milk 5% solution [g/L]	12.42	11.76	11.31	9.36	5.42	4.93
pH before neutralization	5.09	5.09	5.10	5.09	5.08	5.10
pH after neutralization	7.18	7.13	7.64	7.24	7.28	7.78
Parameter of filtrate						
Turbidity [NTU]	<1	<1	<1	<1	<1	<1
Color [mg Pt/L]	141	140	157	159	155	189
pH	7.07	6.86	7.06	6.76	6.80	7.22
COD [mg O_2/L]	3,888	4,435	4,479	4,433	4,452	4,514
P [mg/L]	0.97	0.91	1.14	1.06	0.95	0.99
Kjeldahl nitrogen [mg/L]	615	618	625	641	633	648
Ca [mg/L]	260.00	237.00	260.00	226.00	232.00	264.00
Mg [mg/L]	21.00	22.10	22.10	22.10	23.10	21.70
Fe [mg/L]	<0.180	<0.180	<0.180	0.222	0.222	0.197
Zn [mg/L]	<0.030	<0.030	<0.030	<0.030	<0.030	<0.030
Mn [mg/L]	<0.030	<0.030	<0.030	<0.030	<0.030	<0.030
Ni [mg/L]	<0.070	<0.070	<0.070	<0.070	<0.070	<0.070
K [mg/L]	237.00	248.00	248.00	244.00	254.00	256.00
Cu [mg/L]	<0.080	<0.080	<0.080	<0.080	<0.080	<0.080
Cd [mg/L]	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Cr [mg/L]	<0.090	<0.090	<0.090	<0.090	<0.090	<0.090
Pb [mg/L]	<0.700	<0.700	<0.700	<0.700	<0.700	<0.700
Co [mg/L]	<0.080	<0.080	<0.080	<0.080	<0.080	<0.080

Table 3. Results of physicochemical analysis of MBM wastewater samples treated using the Fenton process, with a constant mass ratio of Fe^{2+}/H_2O_2 – Variant II

Mass ratio	Variant II					
Fe^{2+}/H_2O_2	1:10	1:10	1:10	1:10	1:10	1:10
Doses of reagents/pH						
$FeSO_4 \cdot 7H_2O$ [g/L]	3.0	4.5	6.0	7.5	9.0	10.5
H_2O_2 [g/L]	6.0	9.0	12.0	15.0	18.0	21.0
Lime milk 5% solution [g/L]	15.41	18.78	27.91	35.63	48.20	56.51
pH before neutralization	5.09	4.69	4.31	3.78	3.18	2.82
pH after neutralization	7.17	7.18	7.22	7.10	7.12	7.05
Parameter of filtrate						
Turbidity [NTU]	<1	<1	<1	<1	<1	<1
Color [mg Pt/L]	163	154	145	112	40	37
pH	6.87	6.72	6.54	6.52	6.51	6.53
COD [mg O_2/L]	4,433	3,428	3,367	3,406	3,551	3,493
P [mg/L]	0.84	0.86	0.80	0.85	0.65	0.68
Kjeldahl nitrogen [mg/L]	608	611	593	594	580	583

On the other hand, the iron complexes that were formed during the wastewater treatment process acted as flocculants. The process was intentionally carried out without correcting the pH value of the effluent, so as not to generate additional costs, so it should be mentioned that other degrees of pollution reduction will be obtained in the acidic reaction conditions.

In the Variant I wastewater treatment (Table 2) using the Fenton method, a fixed dose of $FeSO_4 \cdot 7H_2O$ and variable doses of H_2O_2 were used. The mass ratio of Fe^{2+}/H_2O_2 ranged from 1:5 to 1:30 with the change in the H_2O_2 dose.

Analysis of the filtrates showed that with a constant Fe^{2+} dose of 0.60 g/L, regardless of the amount of H_2O_2 added, all turbidity values <1 NTU were obtained. The color intensity of the filtrate was a maximum of 189 mg Pt/L and an increase in the amount of H_2O_2 added resulted in an increase in the color intensity. The lowest COD value was 3,888 mg O_2/L at a Fe^{2+}/H_2O_2 ratio of 1:5. In the remaining samples in this series of tests, despite the increasing doses of the oxidant, no decrease in the COD value was observed, but even its increase. Typically, as the concentration of hydrogen peroxide increases, the degree of pollutant degradation in the wastewater increases; however, too high a dose of hydrogen peroxide may reduce the treatment efficiency. The reactions of the hydroxyl radicals with H_2O_2 or the combination of two hydroxyl radicals reduce the efficiency of the reaction, and the unused amount of excess hydrogen peroxide increases the COD value of the treated effluents.

The content of phosphorus and Kjeldahl nitrogen changed, respectively, in the ranges of 0.91–1.14 mg/L and 615–648 mg/L and it can be concluded that the concentrations of these parameters in the tested samples remain constant despite the differentiated doses of H_2O_2. The increase of the Ca concentration in the analyzed filtrates, compared to its content in the raw wastewater, resulted from the neutralization of the wastewater slurry with lime milk. The pH of all the wastewater samples after the Fenton reaction was approx. 5.0 and, after neutralization with lime milk, it was in the range of 7.13–7.78. However, after filtration, the pH of the filtrates was in the range of 6.76–7.22. The concentrations in the filtrates of zinc, manganese, nickel, copper, cadmium, chromium, lead, and cobalt were below the limit of sensitivity of the apparatus.

In Variant II of the MBM wastewater treatment, variable doses of $FeSO_4 \cdot 7H_2O$ and H_2O_2 were used, with a constant mass ratio of Fe^{2+}/H_2O_2 equal to 1:10 (Table 3). These combinations of reagents allowed all turbidity values <1 NTU to be obtained, as in Variant I, but a significantly lower color intensity was observed, along with an increase in the dose of reagents added. The lowest color intensity of filtrate was 37 mg Pt/L.

In this series of tests (Variant II), both the catalyst and oxidant doses were increased. At the dose of 3.00 g $FeSO_4 \cdot 7H_2O$, it is visible that the purification process is not as effective as at higher catalyst doses, where the COD value is lower by approx. 1000 mg O_2/L. As the dose of $FeSO_4 \cdot 7H_2O$ increases, the COD value decreases, reaching the lowest value of 3.367 mg O_2/L at a dose of 6.00 g $FeSO_4 \cdot 7H_2O$, and a further increase in doses causes an increase in the COD value. The literature reports that the efficiency and speed of the Fenton process increase with increasing ferrous ion concentration, but after exceeding a certain maximum value for the treatment of given wastewater, a further increase in concentration is not advantageous for the process. Too much iron, i.e. more than needed for the wastewater treatment, increases the iron content in the treated wastewater, additionally polluting it.

The concentration of phosphorus in the treated wastewater samples varied in the range of 0.65–0.86 mg/L, and the lowest values were obtained with the use of the highest doses of lime milk in the neutralization process. It was noted that as the doses of Fenton's reagent increased, there was a slight decrease in the concentration of Kjeldahl nitrogen, whose values varied in the range of 611–580 mg/L.

The results for Variant I and Variant II from the Response Surface Method[33] are depicted in Figures 1–5.

Table 4 presents analyses of filtrate after treatment of wastewater with a constant dose of 5 mL/L coagulant PIX 113 and variable doses of H_2O_2 in the range of 3–18 g/L (Variant III).

The test results showed that the increase in the doses of hydrogen peroxide at a constant dose of PIX 113 (7.7 g/L) did not significantly change the turbidity, color, Kjeldahl nitrogen, and phosphorus. The biggest differences are seen in the determination of chemical oxygen demand. In the range of H_2O_2 doses from 3.0 to 9.0 g/L, a decrease in the COD value of the treated wastewater samples is noticeable along with an increase in the oxidant dose, while a further increase in H_2O_2

Table 4. Results of physicochemical analysis of MBM wastewater samples treated using a constant dose of PIX 113 coagulant and variable doses of H_2O_2 – Variant III

Mass ratio	Variant III					
PIX 113/H_2O_2	2.57	1.28	0.86	0.64	0.51	0.43
Doses of reagents/pH						
PIX 113 [mL/L]	5.0	5.0	5.0	5.0	5.0	5.0
PIX 113 [g/L]	7.7	7.7	7.7	7.7	7.7	7.7
H_2O_2 [g/L]	3.0	6.0	9.0	12.0	15.0	18.0
Lime milk 5% solution [g/L]	21.61	29.05	29.93	29.75	28.71	27.96
pH before neutralization	4.17	4.19	4.20	4.19	4.18	4.18
pH after neutralization	7.29	7.10	7.14	7.15	7.25	7.09
Parameter of filtrate						
Turbidity [NTU]	<1	<1	<1	<1	<1	<1
Color [mg Pt/L]	81	86	90	93	90	91
pH	6.66	6.55	6.58	6.62	6.66	6.58
COD [mg O_2/L]	4,274	4,201	4,090	4,293	4,897	4,343
P [mg/L]	1.12	0.92	1.07	1.02	0.87	0.96
Kjeldahl nitrogen [mg/L]	623	608	599	610	585	615

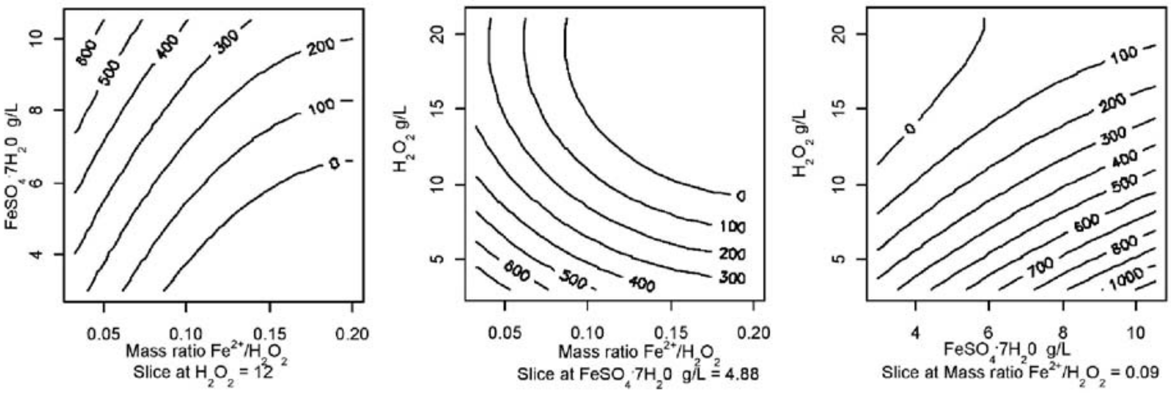

Figure 1. Response surface plots for color [mg Pt/L]

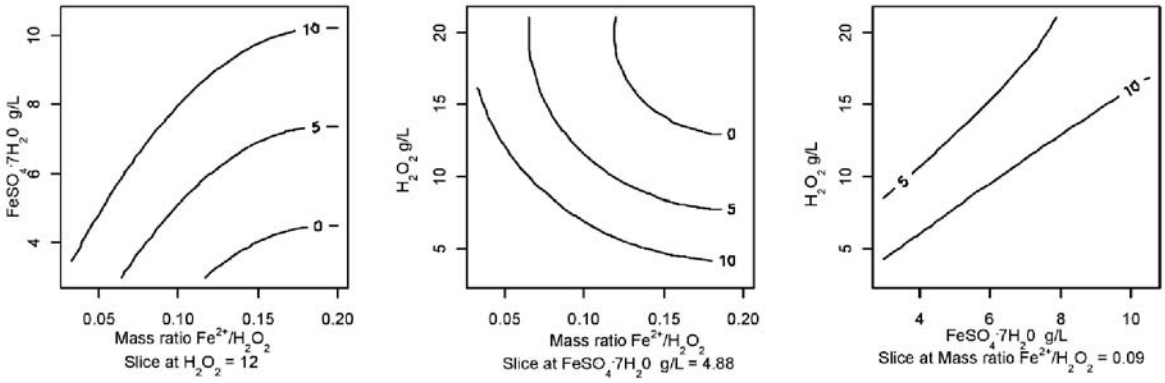

Figure 2. Response surface plots for pH

doses resulted in higher COD values. A similar tendency was observed in Variant I of the study.

Variant IV of the MBM wastewater treatment included variable doses of PIX 113 coagulant in the range of 5–10 mL/L and a constant dose of H_2O_2 10 g/L (Table 5).

The effluent samples treated with variable doses of PIX 113 showed turbidity below 1 NTU regardless of the dose of the coagulant.

The color of the samples varied from 56 to 92 mg Pt /L, with lower values observed in the range of PIX 113 doses from 7 to 9 mL/L. However, it can be noticed that increasing the doses of coagulant resulted in a decrease in the values of COD, phosphorus, and Kjeldahl nitrogen, and the amount of lime milk used, which increased with the dose of coagulant, also influences these relationships.

In Variants III and IV, the coagulant PIX 113 was used; therefore, in the first stage, the coagulation process took place, and then hydrogen peroxide was added to increase the process efficiency. The iron from the coagulant was assumed to be the catalyst for the Fenton process. In both variants, the purification process is positively influenced by the coagulation taking place in the first stage, but it is difficult to determine to what extent it has an impact on the Fenton process, as it is known that the efficiency and speed of this process depend, among others, on the doses of the iron catalyst, and iron salts in aqueous solutions appear in various forms depending on the pH value.

Figure 6 summarizes the degrees of reduction of color, turbidity, COD, and the concentration of Kjeldahl nitrogen and phosphorus in the filtrate depending on the treatment parameters used.

From the results of the tests realized in all the variants described above used for the treatment of wastewater from the production of meat and bone meal, it can be concluded that in each of them an approx. 100% re-

Table 5. Results of physicochemical analysis of MBM wastewater samples treated using a variable dose of PIX 113 coagulant and a constant dose of H_2O_2 – Variant IV

Mass ratio	Variant IV					
PIX 113/H_2O_2	0.77	0.92	1.08	1.23	1.39	1.54
Doses of reagents/pH						
PIX 113 [mL/L]	5.0	6.0	7.0	8.0	9.0	10.0
PIX 113 [g/L]	7.7	9.2	10.8	12.3	13.9	15.4
H_2O_2 [g/L]	10.0	10.0	10.0	10.0	10.0	10.0
Lime milk 5% solution [g/L]	27.55	37.10	45.17	53.31	60.80	68.04
pH before neutralization	4.26	3.86	3.33	2.95	2.81	2.73
pH after neutralization	7.15	7.10	7.11	7.12	7.06	7.07
Parameter of filtrate						
Turbidity [NTU]	<1	<1	<1	<1	<1	<1
Color [mg Pt/L]	85	92	69	56	65	92
pH	6.50	6.50	6.56	6.65	6.66	6.72
COD [mg O_2/L]	4,430	4,373	4,016	4,185	4,051	3,953
P [mg/L]	1.14	1.01	1.08	0.89	0.68	0.71
Kjeldahl nitrogen [mg/L]	623	637	608	573	585	571

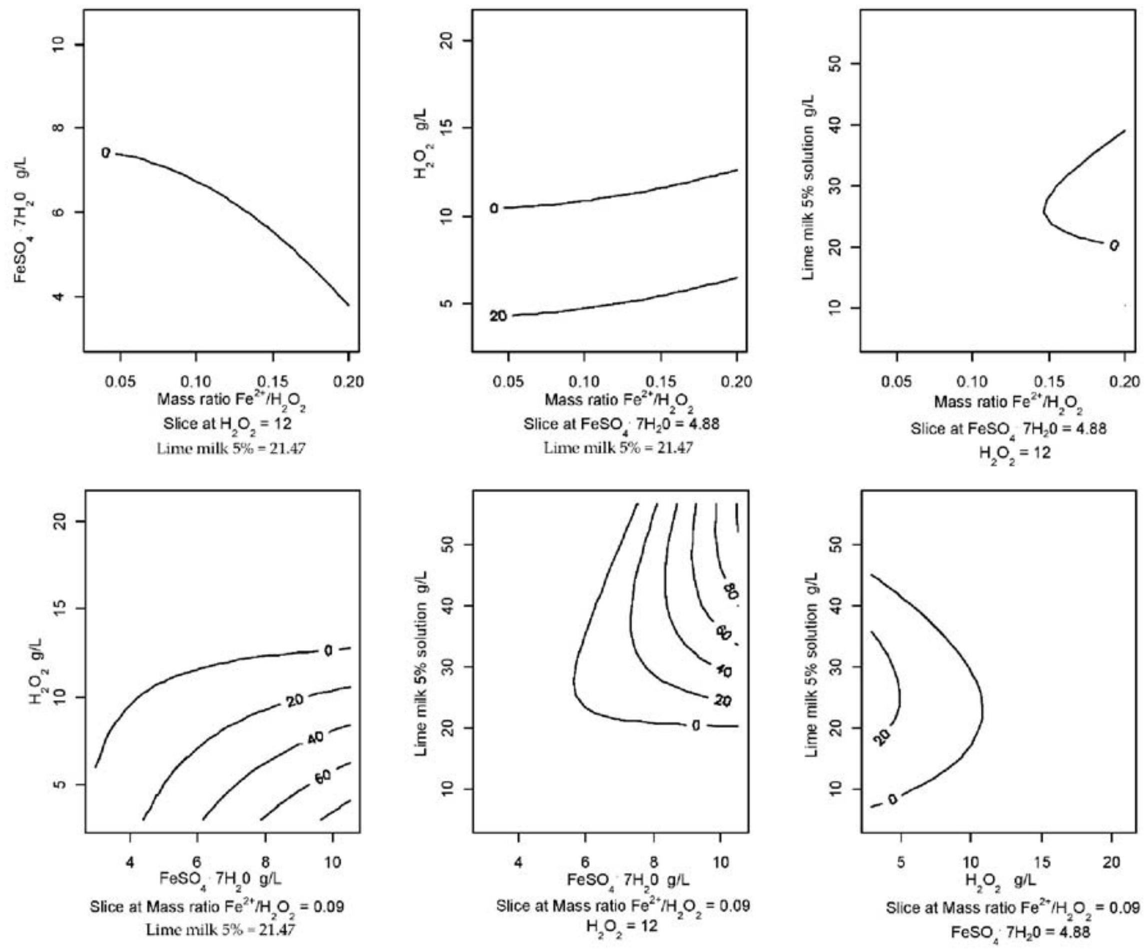

Figure 3. Response surface plots for COD [mg O_2/L]

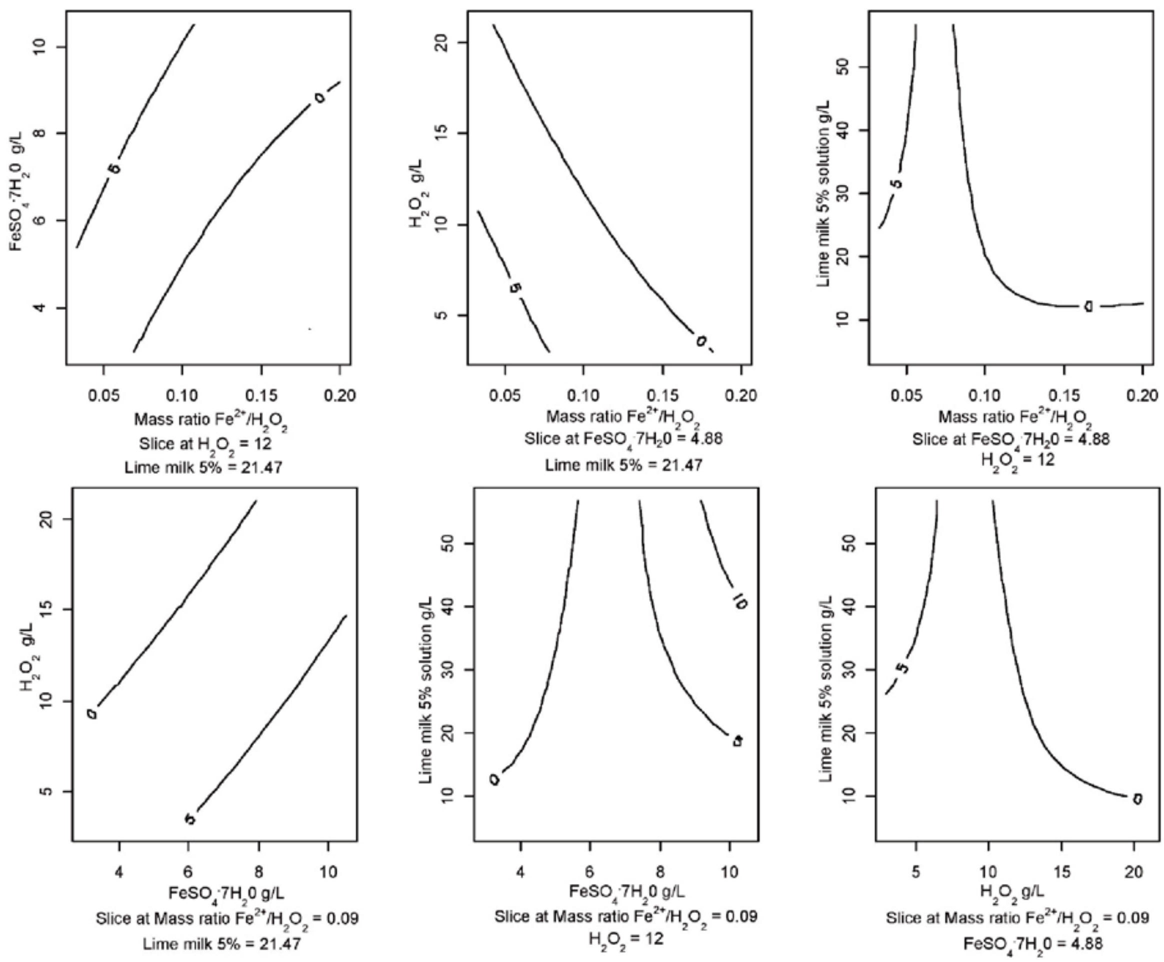

Figure 4. Response surface plots for P [mg/L]

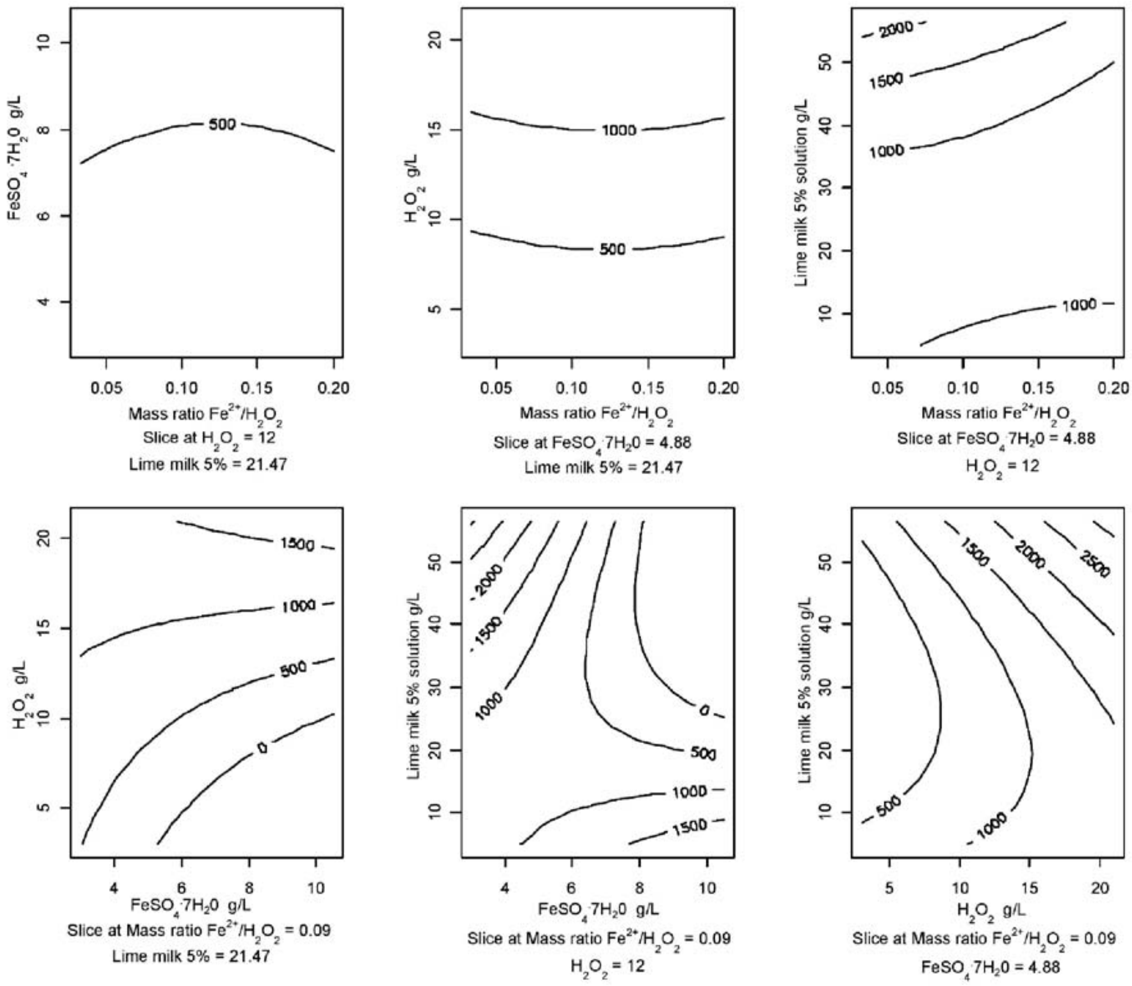

Figure 5. Response surface plots for Kjeldahl nitrogen [mg/L]

duction in turbidity and a 99% reduction in phosphorus content in the tested samples were observed. The highest degree of color reduction, approx. 99%, was achieved in Variant II in the range of $FeSO_4 \cdot 7H_2O$ doses from 9.0 to 10.5 g/L (Fe^{2+}/ H_2O_2 = 1:10). However, in Variants III and IV, where the PIX 113 coagulant was used, the degree of color reduction for all samples was very similar (regardless of the reagent doses) and ranged from 97.2–98.3%. The highest degree of COD reduction at the level of approx. 71% was achieved in Variant II at the dose of $FeSO_4 \cdot 7H_2O$ 6 g/L and the dose of H_2O_2 equal to 12 g/L (Fe^{2+}/H_2O_2 = 1:10). The use of PIX 113 and H_2O_2 coagulant made it possible to reduce the COD to a maximum of approx. 60% (PIX 113 10.4 g/L, H_2O_2 10 g/L). The treatment parameters in Variant IV turned out to be the most effective in reducing Kjeldahl nitrogen and reduced this parameter by about 49%.

The calculated degrees of reduction of the examined pollution indicators showed that, regardless of the variant used, the highest degree of reduction was obtained for the determination of turbidity and phosphorus concentration, followed by the color, COD, and Kjeldahl nitrogen concentration.

The sewage used in the research was characterized by a high value of organic load (COD > 11,500 mg O_2/L) and was collected from the MBM plant, where the last stage of treatment of the produced wastewater is realized in the biological wastewater treatment plant. In most biological wastewater treatment plants, a load of organic pollutants in the wastewater introduced should be adjusted to the capabilities of a specific biological wastewater treatment plant, so it is necessary to apply several stages of treatment. The pretreatment options proposed/used enable a decrease of the content of organic compounds in the wastewater from the MBM before its input into a biological wastewater treatment plant where these are processed further before release into the sewage system, where appropriate permissible values of pollutants in wastewater are also required. The chemical treatment of wastewater, whether using coagulants or Fenton's reagent, always produces sludge that precipitates during the treatment process. In our research, a wide range of reagents was used, so following the obtained COD values, one can choose variants that will allow for lower consumption of reagents and a reduction in the amount of sediment produced.

The COD reduction level obtained in our work (70.8%) was comparable with the COD reduction of 74.6–79.5% by De Sena et al.[21], where meat industry wastewater containing up to 13,000 mg/L COD was treated with three ferric salts used as coagulants in conjunction with four different polymers as flocculants, by batch column flotation. A similar value of COD reduction of 74–82% was obtained in the study by De Sena et al.[25], when the meat wastewater was treated by dissolved air flotation (DAF), followed by advanced oxidation processes (AOPs) using photo-peroxidation (H_2O_2/UV) and photo-Fenton

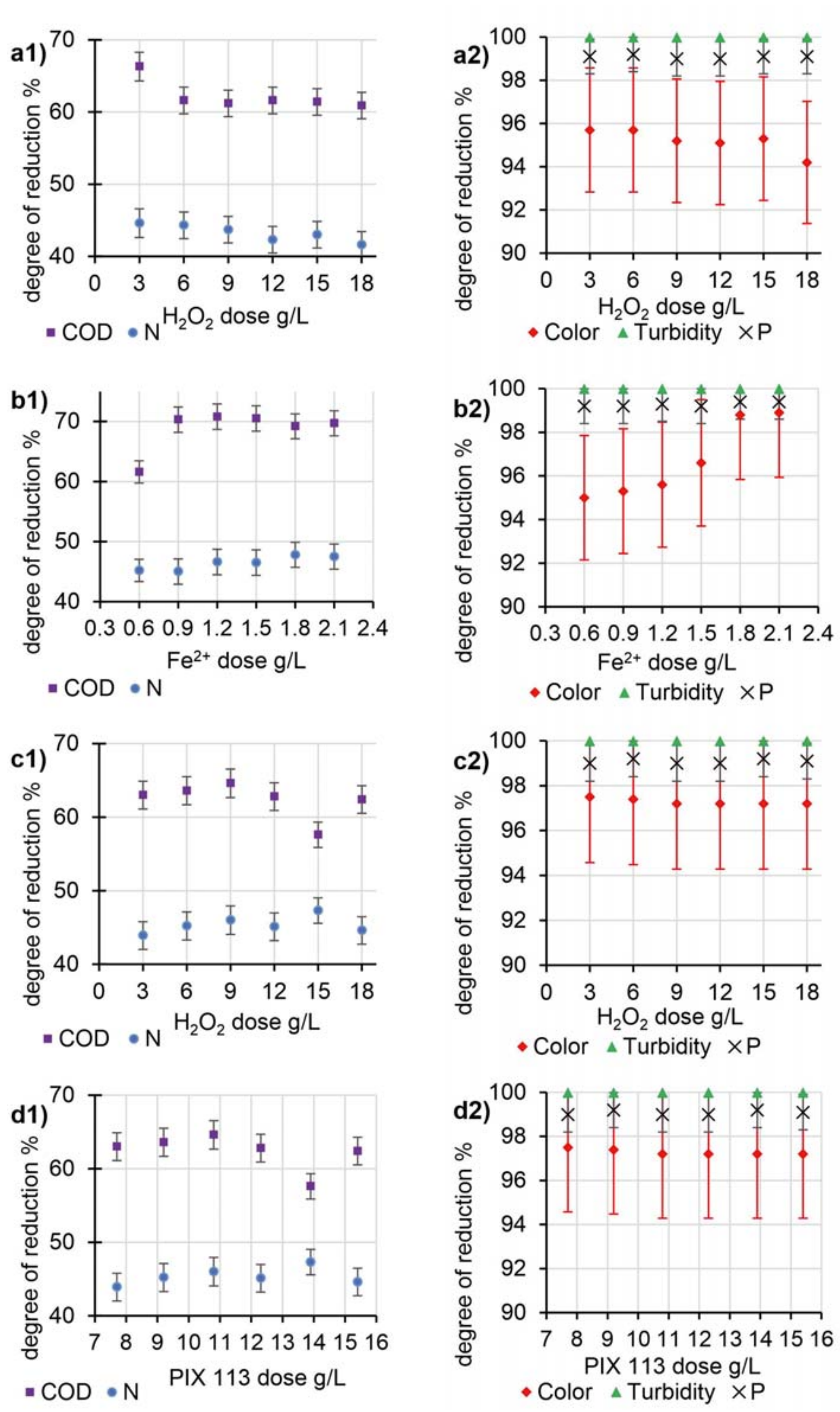

Figure 6. Changes in the degree of reduction of color, COD, turbidity, P and Kjeldahl nitrogen using: a1, a2) Variant I – variable doses of H_2O_2, a constant dose of Fe^{2+} (0.60 g/L) and a variable ratio of Fe^{2+}/H_2O_2; b1, b2) Variant II – variable doses of Fe^{2+} (0.60–2.11 g/L) and H_2O_2 (6.0–21.0 g/L) and a constant ratio of Fe^{2+}/H_2O_2; c1, c2) Variant III – constant dose of PIX 113 (0.77 g/L) and variable doses of H_2O_2 (3–18 g/L); d1, d2) Variant IV – variable doses of PIX 113 (7.7–15.4 g/L) and a constant dose of H_2O_2 (10 g/L). The degree of reduction of turbidity was approximately 100% in all samples (NTU values are not marked in the figures)

reactions. However, both of these compared methods were more complicated.

The morphology of the solid fractions obtained in the process of MBM wastewater treatment was analyzed using scanning electron microscopy. Figure 7 shows SEM images of the surface of selected sediments, and Figures 8 and 9 present the results of the EDS analysis.

The SEM images of the surface of the sediments showed significant diversity in terms of the size and shape of crystallites. Smaller grains with different structures are located on larger crystallites. EDS point analysis of the chemical composition of sediments showed a rather high Fe content of 16–23%, the presence of carbon, oxygen, calcium, phosphorus, and sulfur, and, in lower amounts, zinc, magnesium, aluminum, and silicon.

The characteristics of the sediments are similar to sewage sludge obtained from the biological treatment unit. In the analyzed case, the total amount of sediment

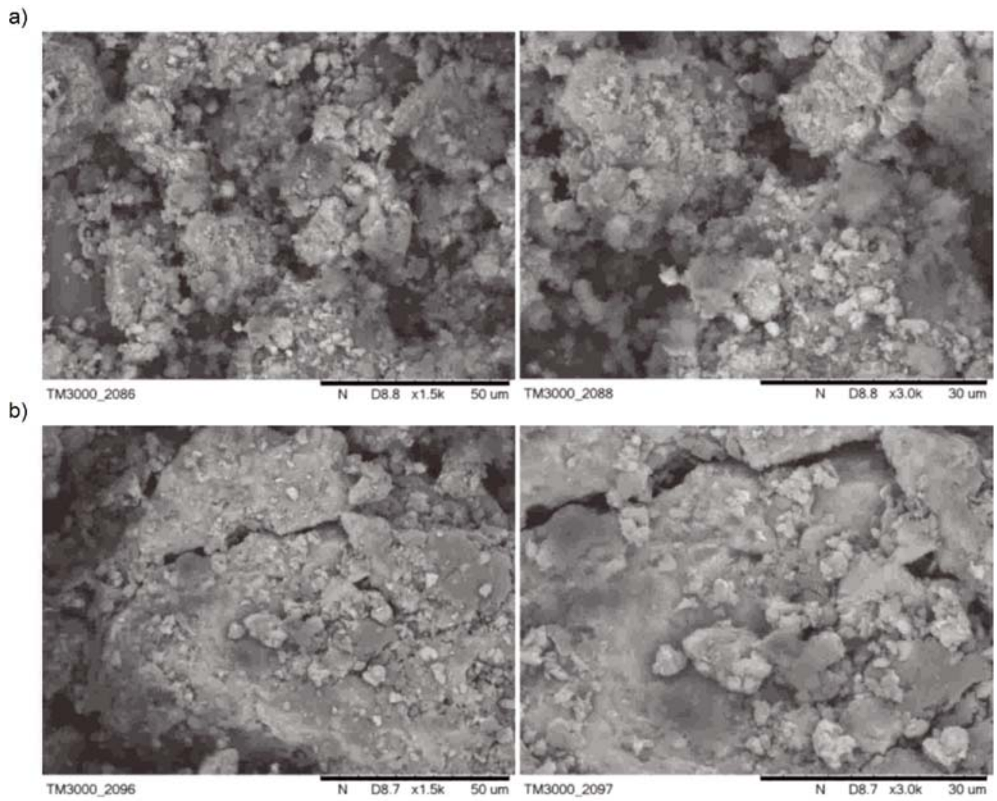

Figure 7. SEM images of sediment obtained as a result of MBM wastewater treatment using a) the Fenton process – Variant II – Fe^{2+}/H_2O_2 = 1:10, 2.11 g Fe^{2+}/L, b) coagulant PIX 113 and H_2O_2 (Variant IV – 10 mL PIX 113/L, 10.0 g H_2O_2/L)

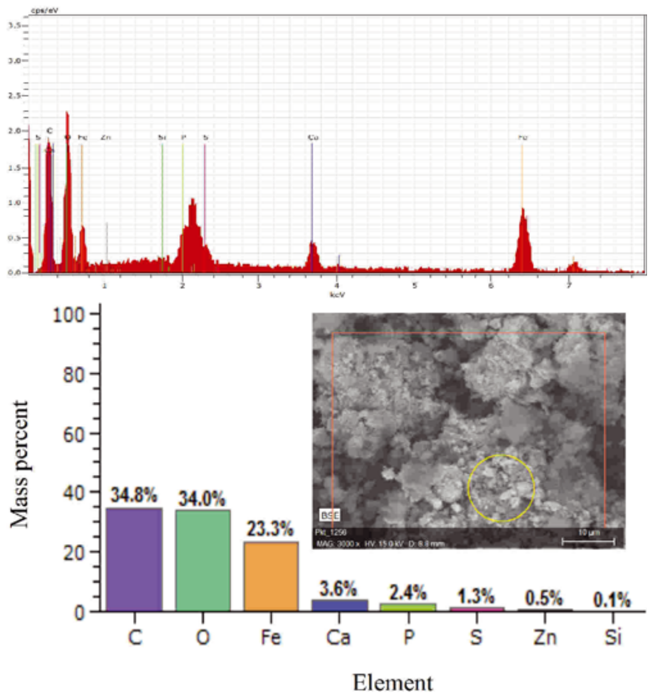

Figure 8. EDS analysis of sediment obtained as a result of MBM wastewater treatment in the Fenton process (Variant II – Fe^{2+}/H_2O_2 = 1:10, 2.11 g Fe^{2+}/L)

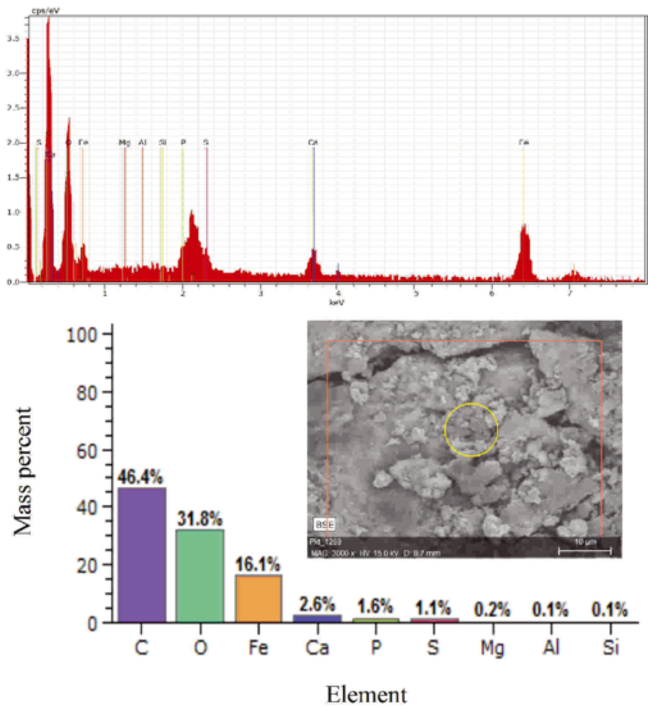

Figure 9. EDS analysis of sediment obtained as a result of MBM wastewater treatment using coagulant PIX 113 and H_2O_2 (Variant IV – 10 mL PIX 113/L, 10.0 g H_2O_2/L)

from the MBM wastewater treatment is estimated to be 0.1% of the mass of treated MBM wastewater.

CONCLUSIONS

Research on the comparison of the effectiveness of the treatment of meat and bone meal industry wastewater with the use of the coagulation process and Fenton's reagent allows the following conclusions to be drawn:

– a combination of these methods, irrespective of the doses of $FeSO_4 \cdot 7H_2O$ and H_2O_2, as well as PIX 113 and H_2O_2, enabled a 100% reduction of the turbidity of the wastewater. A degree of color reduction over 98% can be achieved both with the appropriate combination of doses PIX 113 and H_2O_2 (PIX 113/H_2O_2 = 1.23; 1.39) and with $FeSO_4 \cdot 7H_2O$ and H_2O_2 (Fe^{2+}/H_2O_2 = 1:10, $FeSO_4 \cdot 7H_2O$ in doses 9 g/L and 10.5 g/L).

– in the variants used, the highest efficiency of COD reduction at the level of approx. 70% was obtained using Fe^{2+} doses in the range of 0.9–2.1 g/L and with a ratio of Fe^{2+}/H_2O_2 equal to 1:10.

– the degree of phosphorus reduction was 99% and did not depend on the reagents used or the combination of doses. The highest reduction of Kjeldahl nitrogen concentration in the treated liquid fractions was ~48% for all variants.

The proposed combination of treatment methods could be used as the next (after mechanical separation) treatment stage of wastewater from MBM production, enabling a more effective final biological treatment.

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